



Publication number: **0 564 273 A1**

**EUROPEAN PATENT APPLICATION**

Application number: **93302530.6**

Int. Cl.<sup>5</sup>: **H05H 3/04**

Date of filing: **31.03.93**

Priority: **03.04.92 JP 82525/92**

Date of publication of application:  
**06.10.93 Bulletin 93/40**

Designated Contracting States:  
**BE DE FR GB NL**

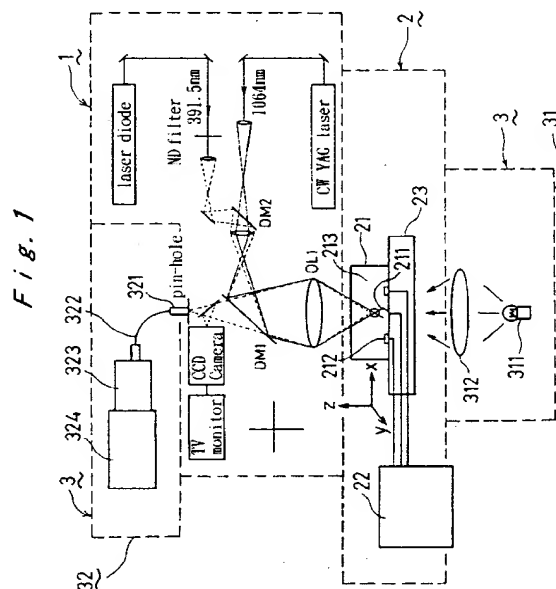
Applicant: **RESEARCH DEVELOPMENT  
CORPORATION OF JAPAN**  
2-5-2, Nagato-cho  
Chiyoda-ku, Tokyo (JP)

Inventor: **Nakatani, Kiyoharu, 103  
Kohpo-Matsunoki  
338-2 Matsunoki-cho, 2-Sujinishiiru,  
Imadegawadori  
teramachi, Kamigyo-ku, Kyoto-shi (JP)**  
Inventor: **Misawa, Hiroaki  
11-2 Kitazono-cho  
Takatsuki-shi, Osaka (JP)**  
Inventor: **Kitamura, Noboru  
502 Mezon-Takano, 34-35  
Kamifurukawa-machi  
Tanaka Sakyo-ku, Kyoto-shi, Kyoto (JP)**  
Inventor: **Uchida, Tatsuya  
206 Arekkusa-Anesaki, 367 Anesaki  
Ichihara-shi, Chiba (JP)**

Representative: **Marsden, John Christopher  
Frank B. Dehn & Co. Imperial House 15-19  
Kingsway  
London WC2B 6UZ (GB)**

**Method and apparatus for effecting reaction of particles.**

Particles are trapped by a laser beam and brought into contact with an electrode to induce an electrochemical reaction, the progress of which may be monitored electrically and spectroscopically, thereby permitting precise measurements of parameters involving single particles.



The present invention relates to a method and apparatus for effecting reactions involving particles. More particularly it relates to a method and apparatus for effecting electrochemical reaction in or of particles, and is useful in such fields as microelectronics, biotechnology and materials science. The invention further embraces methods of monitoring the reaction process, e.g. electrochemically and/or spectroscopically.

In fields such as microelectronics, biotechnology and materials science, it is often necessary to study reactions in micro-regions, and techniques for this purpose have been examined.

In general, however, it is very difficult both to control particle reactions at microparticle level by microscopic techniques and to monitor such particle reactions. Conventional practice has therefore been to use a macroscopic technique, involving a time factor and calculating the desired parameter for a particle from the progress of the reaction(s) over a certain period of time by means of a calculation formula.

However, because of the time factor introduced in this technique and the fact that the reaction(s) cannot precisely be determined in terms of the macroscopic correlation with time, this technique is not suitable for cases requiring accurate measurement.

A method known as laser trapping in which individual particles with sizes of the micrometre order are trapped by a laser beam has been developed by the present inventors, and efforts are being made to expand its scope of application to transportation, combination and reaction of particles, e.g. to manipulation of metal particles and to formation of patterns by groups of particles and subsequent processing thereof. Such laser trapping techniques thus permit non-contact operations such as trapping, migration and processing of particles and groups of particles.

The present invention is based on our finding that laser trapping techniques may be applied in the study of particle reactions, more especially to the study of electrochemical reactions of particles, which term is used hereinafter to embrace both single particles and aggregates of particles, the particle under investigation being controlled by the trapping laser beam.

Thus according to one aspect of the present invention there is provided a method of effecting reaction of particles which comprises trapping a particle by laser beam irradiation and bringing the trapped particle into contact with an electrode so as to induce electrochemical reaction in or of said particle. The ensuing reaction may, for example, be monitored by measuring the quantity of electricity (e.g. as current and/or voltage) passing through the reaction system, which will typically in effect comprise an electrolytic cell. The electrochemical reaction and/or any further reaction induced thereby, e.g. a photochemical reaction, may also be monitored spectroscopically, either simultaneously with or separately from any electrical

measurements. Appropriate monitoring techniques are described in greater detail hereinafter.

In the accompanying drawings, which serve to illustrate the invention without in any way limiting the same:

Fig. 1 illustrates a schematic view indicating apparatus useful in accordance with the present invention;

Fig. 2 illustrates the results of measurement of voltage and current in an example using the method of the present invention; and

Fig. 3 illustrates a plot of fluorescent wavelength and intensity indicating the results of an example using the method of the present invention.

In the apparatus shown in Fig. 1 the symbols represent the following items, respectively:

- 1: laser beam particle manipulator,
- 2: electrochemical reaction detector,
- 21: reaction chamber,
- 211: operating electrode,
- 212: opposite electrode,
- 213: reference electrode,
- 22: potentiostat,
- 23: 3D scanning table,
- 3: photochemical reaction detector,
- 31: light irradiator,
- 311: light source,
- 312: condenser lens,
- 32: photodetector,
- 321: pinhole,
- 322: optical fibre,
- 323: polychrometer,
- 324: electromagnetic radiation detector.

Apparatus of this type, i.e. comprising a laser beam particle manipulator operable in conjunction with an electrochemical reaction detector, advantageously together with photochemical reaction detector means, comprises a further feature of the invention.

The method of the invention provides the ability to control an electrolytic reaction by manipulation of a laser-trapped particle, and to monitor the reaction electrically, e.g. by measuring the total quantity of electricity passed, for example using constant potential electrolysis. Reaction parameters may also be simultaneously or separately monitored by spectroscopic observations involving the particle. In general there is no limitation on the kinds of reaction or nature of particles which may be investigated in accordance with the invention.

In electrical measurements involving the trapped particle, measurement of current and/or voltage or the quantity of electricity passed during the electrochemical reaction permits quantitative determination in the form of numerical values or a graph. Specific applicable techniques include cyclic voltammetry, the potential step method and pulse voltammetry.

It is also possible to measure fluorescence spec-

tra and fluorescent time response with a time resolution of the order of  $10^{-9}$  seconds to  $10^{-12}$  seconds and to measure absorption spectra with a time resolution of the order of  $10^{-6}$  seconds by application of spectroscopic methods.

Fig. 1 illustrates a typical microscopic spectrochemical reaction detector as an example of the present invention. This embodiment comprises a laser beam particle manipulator (1), an electrochemical reaction detector (2), and a spectrochemical reaction detector (3).

In the particle manipulator (1), a CW Nd<sup>3+</sup> YAG laser (wavelength = 1,064 nm) is used as the laser for trapping particles, and a picosecond semiconductor laser (wavelength = 391.5 nm) is used for exciting fluorescence. These laser beams are directed through a lens system towards a microscope (Nikon Optiphot XF) and condensed through a 100-magnification very long operating objective onto the sample.

Particle manipulation is observed through a CCD camera and a television monitor. The position of the laser beams and actual operations are displayed in superimposed form on the monitor screen.

In the illustrated embodiment the electrochemical reaction detector (2) comprises a reaction chamber (21), a potentiostat (22), and a 3D scanning table (23). The reaction chamber (21) has operating electrode(s) (211), an opposite electrode (212), and a reference electrode (213). The potentiostat is connected to the individual electrodes and can provide a potential difference between each electrode.

As the operating electrode(s) (211), a microelectrode or a "large" electrode may, for example, be employed; the former may for example be preferred when electrical measurement is the prime concern, whereas the latter, especially when in transparent form, may be preferred when spectroscopic observations of photochemical reactions are made.

An example of a suitable microelectrode is a gold wire, e.g. having a diameter of 10  $\mu\text{m}$ , which may be insulation-secured with silicone adhesive onto a glass slide, leaving exposed a portion with a diameter of 10  $\mu\text{m}$  and a length of up to 50  $\mu\text{m}$ . Normal working of such an electrode may be confirmed by, for example, CV measurements carried out in a  $10^{-4}$  mol aqueous solution of potassium ferricyanide. Other microelectrodes which may be employed include platinum, silver and semiconductor electrodes, e.g. such as are used for conventional electrochemical purposes.

Suitable "large" electrodes include, for example, SnO<sub>2</sub> transparent electrodes, e.g. having a width of 6mm and a length of 30mm. It will be appreciated that such electrodes may be used in conjunction with electrical as well as spectroscopic measurements and that microelectrodes may also be used when spectroscopic analysis is performed.

The operating electrode may be of any shape and prepared in any suitable way. Thus in addition to the

manually prepared linear microelectrode described above, other methods of preparation may be used, as may other types of electrode, for example band electrodes (e.g. prepared by lithographic techniques) or array electrodes.

Any convenient electrodes, e.g. such as are used for conventional electrochemical purposes, may be used as the opposite electrode (212) and reference electrode (213). Representative opposite electrodes thus include gold electrodes and, more preferably, platinum electrodes. Representative reference electrodes include calomel and, more preferably, silver/silver chloride electrodes.

The 3D scanning table (23) is contact-secured to the bottom of the reaction chamber (21), and is movable three-dimensionally under the action of a power source such as a motor. It is therefore possible to select any particles in the reaction chamber and to manipulate only the selected particle(s) by means of the laser beam particle manipulator.

In the illustrated embodiment the photochemical reaction detector (3) comprises a light irradiator (31) located on the lower surface of the electrochemical reaction detector (2), and a photodetector (32) located on the upper surface of the electrochemical reaction detector (2).

The illustrated light irradiator (31) comprises a light source (311) and a condenser lens (312); light generated from the light source (311) passes through the 3D scanning table (23) and is irradiated onto a sample in the reaction chamber. The light source (311) may, for example, generate visible, infrared or ultraviolet light, e.g. by or to promote fluorescence.

The illustrated photodetector (32) comprises a pinhole (321), an optical fibre (322), a polychromator (323), and an electromagnetic radiation detector (324), such that light transmitted through the sample passes through the pinhole (321) and the optical fibre (322), and is analyzed by the polychromator (323) and the detector (324).

The following non-limitative examples further illustrate the invention.

#### EXAMPLE 1

Using apparatus as illustrated in Fig. 1, an electrochemical reaction was induced using oil drops in an aqueous phase as particles.

The oil drops were prepared by dissolving ferrocene (0.1 mol) as an electroactive substance and tetrabutyl ammonium tetraphenyl phosphate (TBATPE) (0.01 mol) as a hydrophobic support electrolyte in tri-n-butyl phosphat and mixing the resulting oil solution with aqueous KCl (0.2 mol), so that the gravimetric fraction of oil phase was 1%.

A single oil drop was trapped by the laser beam particle manipulator (1) and brought into contact with the operating electrode (211). The potential between

the electrodes was then caused to linear-sweep continuously by means of the potentiostat (22), so as to enable determination of the relationship between electrode potential and current density. The rate of change of electrode potential was 20 mV per second, the electrode potential having an initial value of 0 mV. The reaction was monitored for a period of 40 seconds, and the resulting linear sweep voltammogram (LSV) is shown in Fig. 2.

As is clear from the results shown in Fig. 2, a peak is observed at about 0.5V with a corresponding current of  $1.45 \times 10^{-3}$ A.

Electrochemical reactions of ferrocene and other appropriate compounds such as tetracyanochloridimethane or N,N,N',N'-tetramethyl-p-phenylenediamine may be studied in any manner so far as the compound has an oxidation-reduction potential within a range in which the aqueous phase or other solvent, the oil drop and the particle are not electrolyzed.

The oil drop may comprise any liquid which is not completely miscible with water, such as tri-n-butyl phosphate, nitrobenzene or benzyl alcohol. Alternatively one may use particles of a polymer such as polystyrene or polymethyl methacrylate.

#### EXAMPLE 2

Chemical reactions were simultaneously observed using constant potential electrolysis and spectroscopic measurements to determine approximately the extent of electrolysis and the electrolytic rate.

A fluorescence spectroscopic method was used. The sample in the reaction chamber comprised an aqueous phase and oil drops as used in Example 1, except that 9, 10-diphenylanthracene (DPA) ( $5 \times 10^{-3}$  mol) was additionally dissolved in the oil.

An SnO<sub>2</sub> transparent electrode was used and oil drops were brought into contact therewith using the laser beam particle manipulator.

Measurement of LSV with the SnO<sub>2</sub> electrode as in Example 1 indicated a peak at a potential close to that in Fig. 2, dependent on the potential sweep rate. With the potential kept at 0.6V, oil drops in contact with the SnO<sub>2</sub> electrode, having a diameter of 25  $\mu$ m, were subjected to fluorescent analysis. This gave the relationship between the fluorescence wavelength and the fluorescent intensity, with the constant potential electrolytic time as a parameter. The results are as shown in Fig. 3, where the abscissa represents the fluorescence wavelength, and the ordinate represents the fluorescent intensity: (a) is before electrolysis, (b) is 425 seconds after electrolysis, and (c) is 825 seconds after electrolysis.

It will be seen that the fluorescent intensity of DPA increases as the electrolysis proceeds, apparently because fluorescence of DPA is inhibited by ferrocene and thus increases with the decrease in concentration of ferrocene in the oil drops as it is elec-

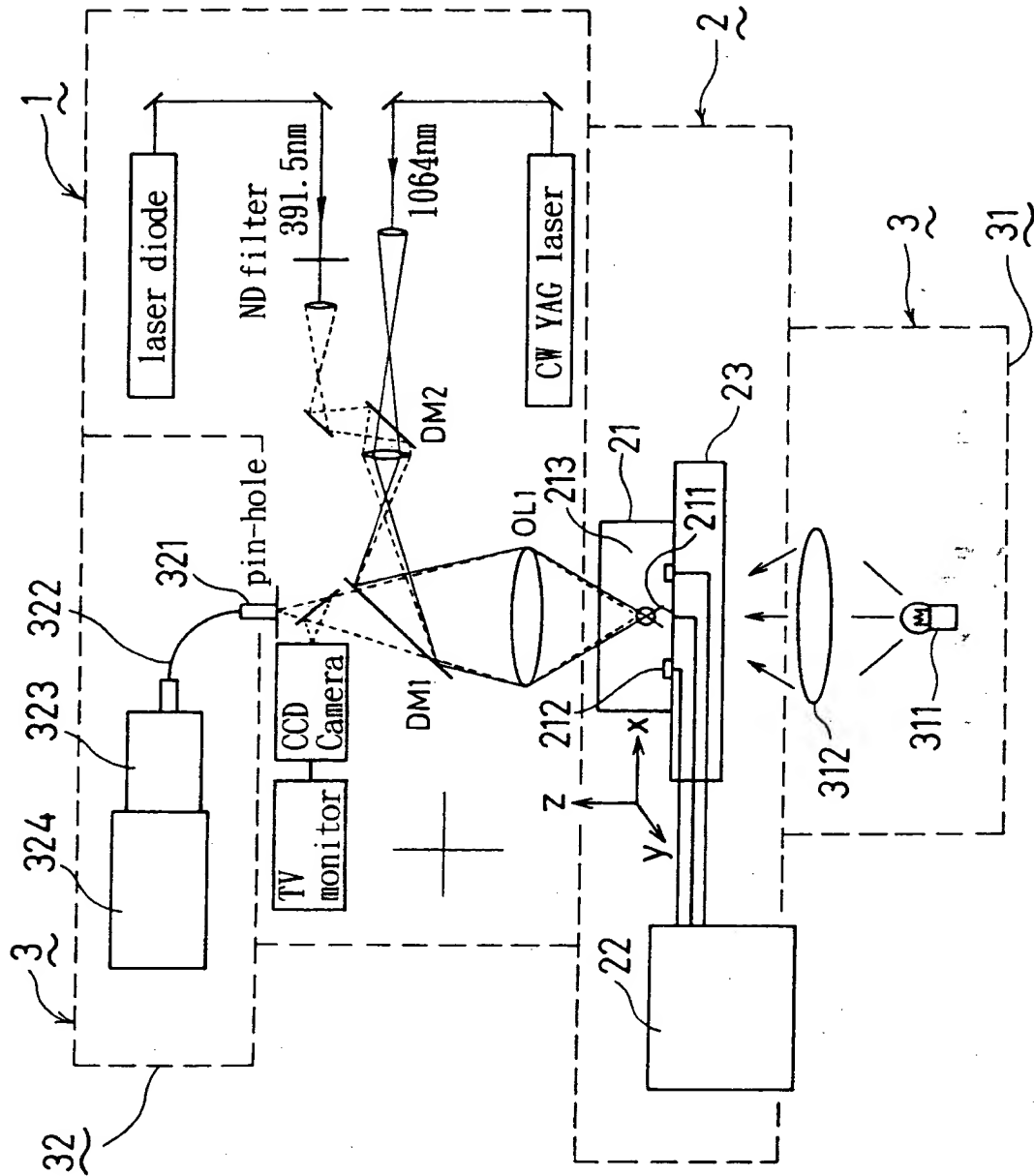
trolyzed.

By using such a fluorescent probe, it is possible to estimate the rate of electrolysis in the oil drops. With the SnO<sub>2</sub> transparent electrode, substantially complete electrolysis of ferrocene in the oil drops required a period of almost 1,000 seconds. However, since this may be attributable to the low electron migration rate of such an electrode as compared with that of a gold electrode, electrolysis is estimated to require a shorter period, i.e. about 300 seconds at most, with a gold microelectrode.

#### Claims

1. A method of effecting reaction of particles which comprises trapping a particle by laser beam irradiation and bringing the trapped particle into contact with an electrode so as to induce electrochemical reaction in or of said particle.
2. A method as claimed in claim 1 wherein the electrochemical reaction is monitored electrically.
3. A method as claimed in claim 2 wherein the current and/or total quantity of electricity passing between the electrode and an opposite or reference electrode and/or the voltage across said electrodes are measured.
4. A method as claimed in any of the preceding claims wherein the electrochemical reaction and/or any further reaction induced thereby are monitored spectroscopically.
5. A method as claimed in claim 4 wherein a fluorescent probe is employed to irradiate the particle and the resulting fluorescence spectrum is monitored.
6. Apparatus of use in the method of claim 1 comprising a laser beam particle manipulator operable in conjunction with an electrochemical reaction detector.
7. Apparatus as claimed in claim 6 further incorporating photochemical reaction detector means.

Fig. 1



*Fig. 2*

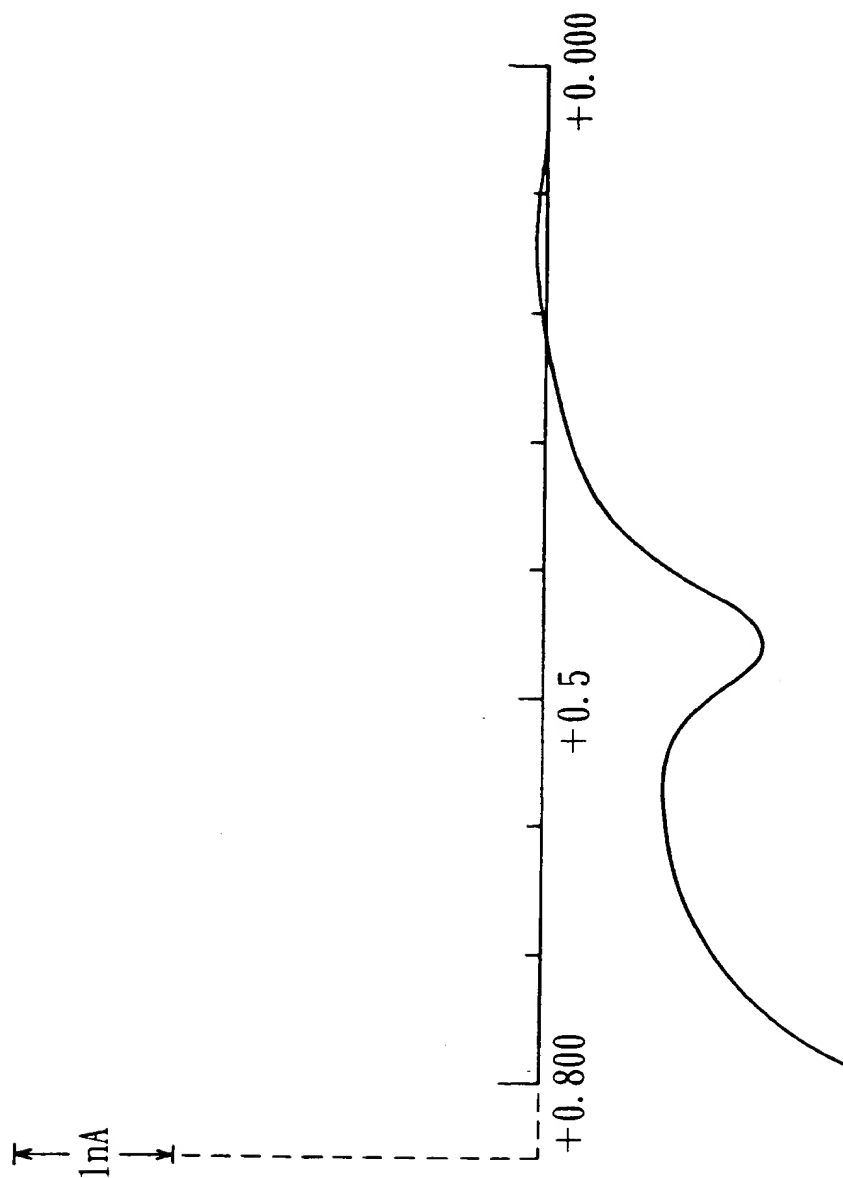
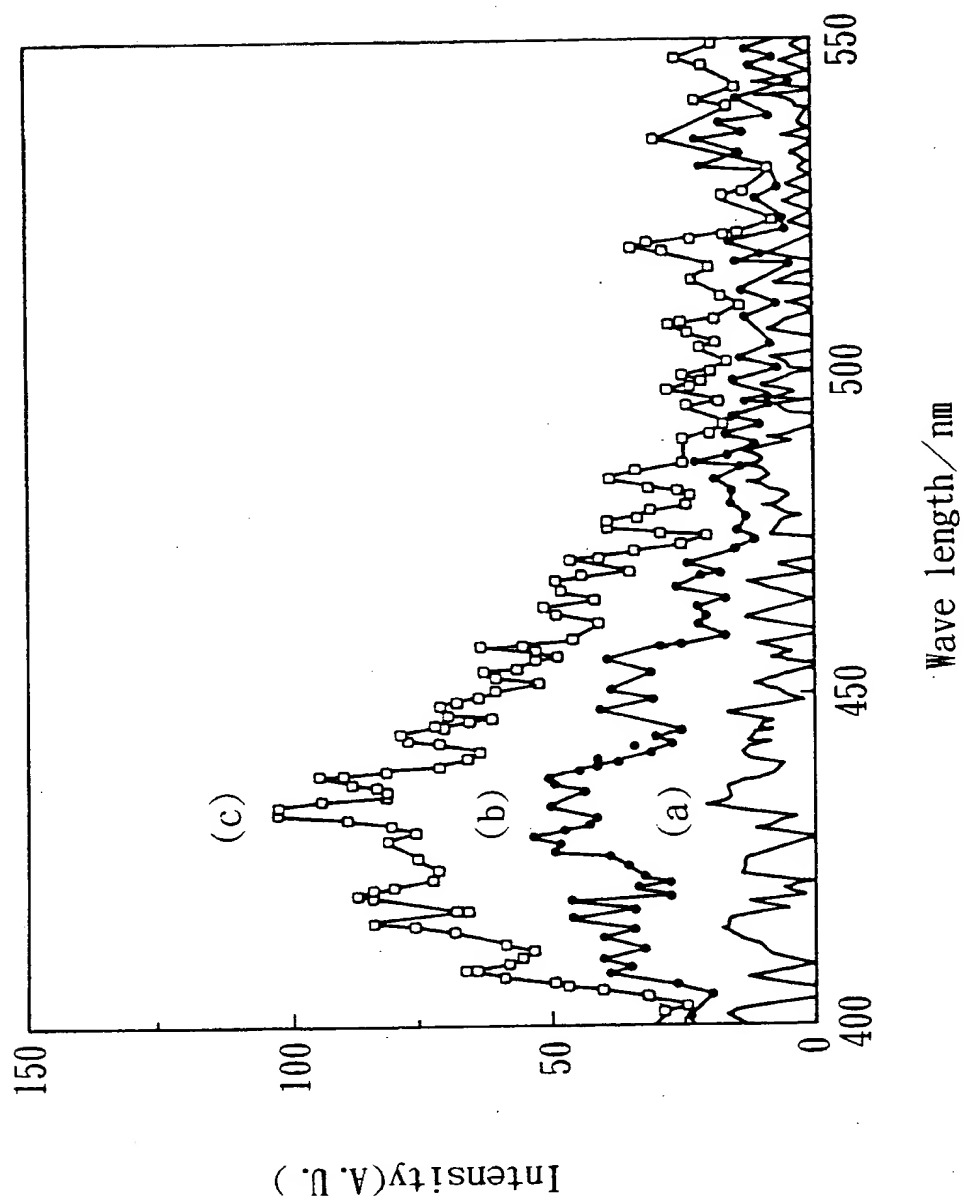


Fig. 3





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 93 30 2530

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-5 100 627 (BUICAN) * abstract *	1	H05H3/04
Y	* column 3, line 23 - line 31 *	4,5	
A	* column 4, line 33 - line 58 *	6	
Y	--- CHEMISTRY LETTERS 1990, TOKYO JP pages 1479 - 1482 H. MISAWA ET AL 'Laser trapping, spectroscopy and ablation of a single latex particle in water' * page 1481, line 1-3 *	4,5	H05H H01S
A	--- JOURNAL OF APPLIED PHYSICS vol. 70, no. 7, 1 October 1991, NEW YORK US pages 3829 - 3836 H. MISAWA ET AL 'Three-dimensional optical trapping and laser ablation of a single polymer latex particle in water' * figure 1 *	1,6	
A	--- OPTICS LETTERS vol. 16, no. 19, 1 October 1991, WASHINGTON US pages 1463 - 1465 K. SASAKI ET AL 'Pattern formation and flow control of fine particles by laser-scanning micromanipulation' -----		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07 JULY 1993	Examiner THOMAS R.M.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- &amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.82 (P0601)